III.A.28 Resilient Sealing Materials for Solid Oxide Fuel Cells

Objectives

- Develop silicate-based glasses with requisite properties to be used for hermetic seals for solid oxide fuel cells (SOFCs).
- Characterize the properties of composite sealing materials prepared by adding fillers to base sealing glasses.
- Demonstrate hermeticity and materials compatibility for seals under SOFC operational conditions.

Accomplishments

- Formulated new alkaline earth silicate glass–ceramic compositions with requisite thermal properties, including sealing temperatures at or below 900°C and coefficients of thermal expansion (CTE) in the range $10\text{-}12 \times 10^{-6}/^{o}C$.
- Developed processing procedures for preparing composite SOFC sealing materials (tapes and pastes), with and without ceramic and metallic filler materials to modify CTE behavior.
- Developed new differential thermal analytical (DTA) techniques to characterize the effects of filler materials on glass crystallization kinetics.
- Produced seals between SOFC components using new materials that remain hermetic after ten thermal cycles between 800°C and room temperature.

Introduction

Reliable hermetic sealing technologies must be developed in order to achieve the high power densities possible for solid oxide fuel cells (SOFC) stacks. For the past decade, considerable effort has gone into the development of glasses and glass-ceramics for these seals (see Fergus, [1], for a recent review). Compositions with the requisite thermal properties for seals have been developed, but questions about long-term property stability, deleterious interfacial reactivity, and component volatility make the development of new, reliable sealing materials a priority.

One concern with the use of 'rigid' glass or glass-ceramic hermetic SOFC seals is the brittle nature of the materials and the consequences of their mechanical failure. Lacking the 'resiliency' of polymers or metals, rigid glasses must be engineered with tight CTE tolerances to avoid the development of catastrophic thermal stresses during thermal cycling. The use of composite materials could enhance the fracture toughness of the seals, and the development of compositions with a stable glassy (viscous) phase with a glass transformation temperature (T_g) below the operational temperature could provide a means (i.e., viscous flow) for 'healing' cracks that form in the seal as a result of thermal stresses. These approaches are presently under study by various groups supported by the DOE (e.g., University of Cincinnati/Raj Singh, NexTech/Matt Seabaugh) and similar ideas were also explored in the present project.

Richard K. Brow (Primary Contact),
Signo T. Reis, Teng Zhang, Mary Reidmeyer
University of Missouri-Rolla
Department of Materials Science & Engineering
222 McNutt Hall
Rolla, MO 65409-0330
Phone: (573) 341-4401; Fax: (573) 341-6934
E-mail: brow@umr.edu

DOE Project Manager:
Ayyakkannu Manivannan
Phone: (304) 285-2078
E-mail: Ayyakkannu.Manivannan@netl.doe.gov

Approach

The glasses developed at the University of Missouri-Rolla (UMR) have relatively low silica contents (<45 mole%) with molecular-level structures that are much less connected than conventional silicate glasses, allowing the melts to readily flow at relatively low temperatures before crystallizing to form glass-ceramic phases with the desired thermal properties. Some compositions were designed to fully-crystallize to form rigid glass-ceramic seals, and others were designed to retain a significant fraction of a glassy phase after crystallization to allow viscous relaxation of thermal stresses. Base glasses were mixed with filler materials (metal and ceramic powders) to tailor CTE and to modify the mechanical behavior of the sealing material.

Results

Over fifty glass compositions have been prepared and evaluated. Many of the compositions have the requisite thermal properties required for SOFC seals (e.g., CTE match to SOFC components and sealing temperatures at or below 900°C) and have received closer examination for their suitability as potential sealing materials. Figure 1 shows how one compositional variation affects the CTE of crystallized sealing glasses. In this case, increasing the relative

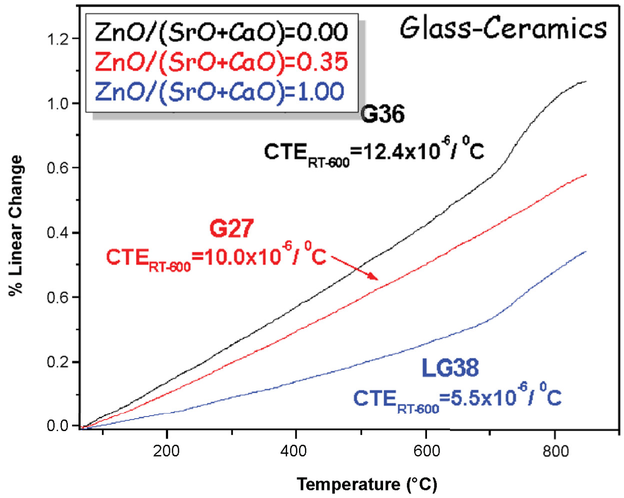

FIGURE 1. Coefficient of Thermal Expansion (CTE) Curves for Several UMR Sealing Glass-Ceramics as a Function of Relative ZnO-Contents

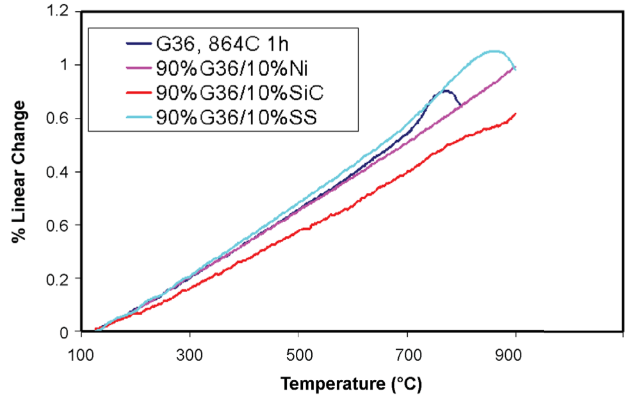

FIGURE 2. CTE Curves for Glass 36 Composites Made with 10 vol% of Ni, SiC, and 304 Stainless Steel Powders, Compared with the CTE Curve of Glass 36 Sintered at 864°C for One Hour

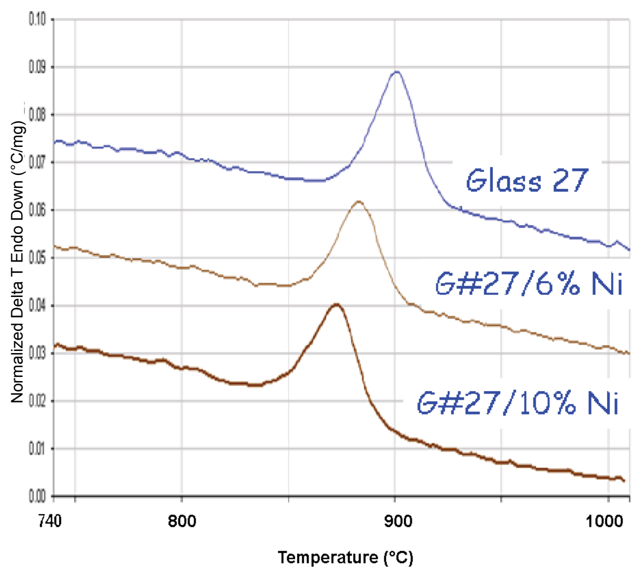

FIGURE 3. DTA Traces from Glass 27 with up to 10 vol% Ni Powder Added

ZnO content of the base glass decreases the CTE of the crystallized material, through the formation of lower expansion Zn-silicate phases, including Zn_2SiO_4. Glass 27 is fully crystallized after several hours at 850°C, whereas a significant residual glassy phase remains in glass 36, as indicated by the break in CTE near 700°C (the glass transition temperature, T_g, of the residual glass) and the dilatometric softening behavior near 800°C. Evidence for residual glass remains in monolithic samples of glass 36 after four weeks at 750°C.

The presence of an apparently stable residual viscous phase makes glass 36 an interesting candidate as a base composition for composite seal formulations. A variety of different filler materials with different expansion coefficients and elastic moduli were added (10 vol%) to the base glass by a ball-milling/mixing technique and these mixtures were sintered to form dense samples that were then evaluated. Figure 2 shows the CTE curves for composites made with Ni, SiC and 304 stainless steel powders. The 'bulk' CTE of the composite material can be tailored over a range of values with the use of different filler materials.

The effects of filler materials on the crystallization behavior of composite sealing materials were studied by a differential thermal analysis technique developed at UMR [2]. By considering changes in the areas of crystallization exothermic peaks from DTA analyses of glass samples following isothermal heat treatments, the fraction of glass crystallized can be measured. Figure 3 shows the DTA responses of glass 27 with and without 6 or 10 vol% Ni. Increasing Ni-contents cause the crystallization exotherm to shift to lower temperatures, an indication for enhanced crystallization kinetics. This is confirmed by a quantitative DTA crystallization study, the results of which are summarized in Figure 4. This figure shows, for example, that at 800°C, glass 27 with 10 vol% Ni is completely crystallized after two hours, whereas 'pure' glass 27 is only about half-crystallized after 12 hours in the absence of this filler phase.

Rapid crystallization of composite sealing materials occurred for all glasses studied. For example, the CTE data for glass 36 in Figure 2 shows that the T_g and dilatometric softening points for the composite materials are much less evident (or nonexistent) compared with the pure glass after similar sintering treatments. These results indicate that the long-term stability of a residual viscous-phase in a composite seal will be difficult to achieve, at least in the glass-forming systems under investigation. As a result, the UMR program has concentrated on the development of optimized 'rigid' glass-ceramic sealing materials.

One promising sealing composition is glass 50. This ZnO- and BaO-free glass crystallizes to form $Sr_2Al_2SiO_7$ and $CaSrSiO_4$ major phases in a material with a CTE of $11.5x10^{-7}$/°C that does not change after 100 days at 800°C. A series of simple seals have been fabricated using glass 50 and their hermeticity has been tested at room temperature using helium gas. The seals were fabricated using glass tapes (PVB binder, 10 µm glass particles) fired in air to 850-900°C, between 430SS as the interconnect material and either YSZ (electrolyte) or Ni-YSZ (anode) substrates. These test samples were heated to 800°C at 2°C/minute in different atmospheres, held for 24 hours, then cooled to room temperature (-2°C/minute) where they were tested for hermeticity using helium gas at 2 psig. Samples that did not leak (hold 2 psig for four hours) were reheated for another 800°C/24 hour heat treatment, and cycled back to room temperature for another hermeticity measurement. Table 1 summarizes the results of some of these tests. Glasses fabricated both at UMR and by a commercial vendor have been evaluated.

TABLE 1. Summary of thermal cycling/hermeticity tests on sealed components. All tests were done using helium at room temperature, following the thermal treatment indicated.

Sealing materials	Test conditions	Number of cycles	Notes
430SS/ glass 50/YSZ	800°C, 24 hours, wet forming gas	10	Still on test; glass prepared at UMR
430SS/ glass 50/Ni-YSZ	800°C, 24 hours, wet forming gas	4	Still on test; glass prepared at UMR
430SS/ glass 50/Ni-YSZ	800°C, 24 hours, air	10	Still on test; glass prepared at UMR
430SS/ glass 50/YSZ	800°C, 24 hours, air	9	Failed after ninth cycle; glass prepared by commercial vendor
430SS/ glass 50/Ni-YSZ	800°C, 24 hours, wet forming gas	4	Failed after fourth cycle; glass prepared by commercial vendor

Conclusions and Future Directions

- Promising sealing glass compositions have been developed and evaluated.
- Hermetic seals have been fabricated and tested at room temperature after thermal treatments at operational temperatures.
- Glass crystallization kinetics have been evaluated using new DTA techniques.
- Optimize glass compositions for commercial suppliers and commercial processing techniques.

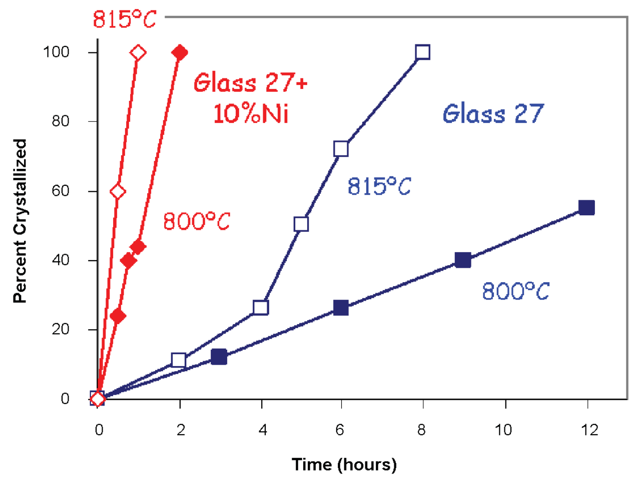

FIGURE 4. Crystallization Kinetic Isotherms for Glass 27 with and without 10 vol% Ni Added

- Characterize viscosity and creep properties of sealing glasses.
- Complete characterization of long-term, high temperature interfacial reactions between glasses and SOFC components.
- Produce and characterize 'at temperature' hermetic seals between SOFC component materials using new glasses.

Special Recognitions & Awards/Patents Issued

1. R.K. Brow, S. T. Reis, G. M. Benson, "Glass and glass-ceramics for solid oxide fuel cell hermetic seals," US Patent Application, UM Disclosure No. 04UMR023 entitled "Glass and Glass-Ceramic Sealant Compositions," filed January 2005.

FY 2006 Publications/Presentations

1. S.T. Reis, R.K. Brow, "Designing Sealing Glasses for Solid Oxide Fuel Cells," Journal of Materials Engineering and Performance, 15[4], XXX-XXX, (2006)- (Proceedings of the ASM Materials Solution Conference, Fuel Cells: Materials, Processing and Manufacturing Technologies, Columbus, OH Oct. 18-20, 2004).

2. T. Zhang*, S. T. Reis, R. K. Brow, and C.S. Ray, "Crystallization Studies of SOFC Sealing Glasses," 3rd International Symposium on Solid Oxide Fuel Cell: Materials and Technology, 30th International Conference & Exposition on Advanced Ceramics & Composites, Cocoa Beach, FL, Jan. 22-27, 2006.

3. S.T. Reis*, R.K. Brow, and T. Zhang, "Glass-Ceramic Seals for Solid Oxide Fuel Cells: Thermo-Phase Stability," 3rd International Symposium on Solid Oxide Fuel Cell: Materials and Technology, 30th International Conference &

Exposition on Advanced Ceramics & Composites, Cocoa Beach, FL, Jan. 22-27, 2006.

4. S.T. Reis, R.K. Brow. P. Jasinski, and T. Zhang, "Properties of Glass-Ceramic Seals for Solid Oxide Fuel Cells," proceedings of the 3rd International Symposium on Solid Oxide Fuel Cells, 30th International Conference & Exposition on Advanced Ceramics & Composites, Cocoa Beach, FL, Jan. 22-27, 2006.; accepted for publication by the American Ceramic Society, 3/14/06.

5. T. Zhang, C.S. Ray, S.T.Reis, and R.K. Brow, "Isothermal Crystallization of Solid Oxide Fuel Cell Sealing glass by Differential Thermal Analysis," J. Amer. Ceram. Soc. (in preparation).

References

1. J.W. Fergus, *J. Power Sources*, 147 46-57 (2005).

2. C. S. Ray, T. Zhang, S. T. Reis and R. K. Brow, "Determining Kinetic Parameters for Isothermal Crystallization of Glasses," *Nucleation and Crystal Growth in Glasses and Liquids*, (submitted).